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MICROSTRUCTURAL INVESTIGATION OF $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R = Y, Gd, Nd)

by

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ABSTRACT

$\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ perovskites, where R is Y, Gd and Nd, were synthesized using the same experimental conditions. The resistivity curves of the three compounds were similar but their microstructures were different. Secondary phases (CuO , BaCuO_2) were formed in the compounds containing Y and Gd while no such phases were detected in the Nd perovskite material.

1 - INTRODUCTION

The cuprate perovskites $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$, where R is Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Tm, Yb and Lu, show a superconducting transition temperature ($T_c = 90$ K) which is nearly non related to the nature of the R atom [1,2]. It is explained by the fact that the R atom does not modify the structure of the superconducting layers but only the distance between them [3]. However, this slight modification of the crystal structure may change the reactivity and stability of these compounds. Some preliminary observations concerning the microstructure of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where R is Y, Gd and Nd are reported here.

2 - EXPERIMENTAL

Superconducting compounds were prepared by mixing the appropriate amount of CuO , BaCO_3 , Y_2O_3 , Gd_2O_3 and Nd_2O_3 , each of 99,999% purity. The different mixtures were heated at 950°C for 12 hours in an alumina crucible and the resulting compacts were crushed and sieved to pass through a 400 mesh screen. The heating and crushing steps were repeated a second time, and green pellets were pressed at a pressure of 390 MPa.

Green pellets were thereafter sintered at 950°C for 6 hours, cooled to 500°C in 1 hour and held at this temperature for 2 hours and finally, cooled to room temperature in about 2 hours. All the thermal treatments were made under a flowing oxygen atmosphere.

Resistivities were measured using the conventional four probe method with silver paint contacts. Temperature measurements were accurate within ± 1.0 K. X-ray diffraction (XRD) analysis was done using the CuK_α radiation. Differential thermal analyses (DTA) were done on all different powders in an alumina crucible using a Setaram Model B70 system. The heating rate was 10 degrees/min and the atmosphere was pure oxygen.

3 - RESULTS AND DISCUSSION

The resistivity-temperature curves for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ sintered pellets are shown in Figure 1. The samples containing Y, Gd and Nd show an abrupt decrease in resistivity (T_{onset}) starting at 92.0, 93.5 and 95.0 K, respectively. The values of T_{onset} , the temperature at the midpoint of the transition (T_{midpoint}) and the temperature at which the resistivity is zero are given in Table I for the three compounds. The narrowest transition width is 2 K, and is obtained with the Nd compound. These values are similar to those already reported [2-3].

X-ray diffraction patterns of the three powders obtained after the second heat treatment were similar. Only small shifts in peaks position reflecting small changes in unit cell dimensions can be observed. The X-ray diffraction patterns of sintered pellets obtained directly from the surface of pellets are shown in Figure 2. The surface analysis of the Y pellet shows an increase of (002), (003), (005) and (006) plane reflections. This result indicates that the microcrystals near the pellet surface have a preferential orientation. Therefore the c-axis tends to be oriented perpendicularly to the pellet surface. This orientation of the c-axis was not observed in $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ or $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ pellets.

The metallographic cross-section of sintered pellets are shown in Figure 3. All the pellets contain porosity at some extent (black spots in micrographies). The twinned crystals are larger in sintered pellets containing yttrium ($80 \times 20 \mu\text{m}$) than in Gd ($10 \times 10 \mu\text{m}$) and Nd ($20 \times 10 \mu\text{m}$) ones. As revealed by energy dispersion X-ray analysis, minor phases are present in the pellets containing Y and Gd. One of these phases, located at the interface of large yttrium crystals was found to contain copper. The amount of minor phases in the Nd pellet is thought to be lower since microstructure examination failed to detect them.

Thermograms of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$, and $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ fine powders ($38 \mu\text{m}$) are shown in Figure 4. All the peaks observed between 800°C and 1200°C correspond to endothermic reactions. From the DTA curve of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder, an extrapolated onset temperature of 1030°C is obtained for the most important peak. This temperature is in good agreement with the previously reported one of 1035°C [4] for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. This peak has been identified as the incipient melting of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. It corresponds to the incongruent melting of $\text{Y}_2\text{Ba}_1\text{Cu}_3\text{O}_{7-\delta}$ into solid $\text{Y}_2\text{Ba}_1\text{Cu}_1\text{O}_5$ and liquid phases [5]. According to Roth [5], the system is entirely liquid at $1258 \pm 2^\circ\text{C}$. The substitution of Y by Gd or Nd changes the temperature at which the liquid is formed. The extrapolated onset melting temperatures are 1075°C and 1107°C for $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ respectively. These differences in temperature indicate that the phase diagrams of compounds containing Gd and Nd are different from the ones of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Information on the presence of secondary phases can be also obtained from DTA curves. The peak temperature of 1000°C obtained only with the $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder corresponds very well with the melting temperature reported for BaCuO_2 [6]. Moreover, the presence of this phase was confirmed by X-ray diffraction analysis. The peak at about 810°C , observed in the powder, corresponds to the transformation temperature of BaCO_3 into the hexagonal β -form [7]. The presence of BaCO_3 in this powder was confirmed by the Fourier transformed infrared spectroscopy. Other

weak peaks were also observed at about 935°C, 970°C and 1035°C in DTA curves of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powders but no interpretation has been done yet.

The presence of secondary phases (BaCuO_2 , BaCO_3) in the $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder shows that a certain amount of BaCO_3 reacts with Gd_2O_3 and CuO , an other amount reacts only with CuO and a last amount does not reacts at all. It is the equilibrium conditions that dictate what could be stable phases in a system at a certain temperature [5]. The substitution of only one component in the system causes modifications in the equilibrium conditions. Different secondary phases are then obtained when synthesizing of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ containing Y_2O_3 , Gd_2O_3 or Nd_2O_3 . At 950°C, it ensues from this study that the Nd-Ba-Cu-O system is more favorable to the formation of the 123 compound than the Y-Ba-Cu-O system and than the Gd-Ba-Cu-O system.

CONCLUSIONS

Even if the resistivity curves of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds are very similar, their synthesis and sintering differently proceed. The three perovskites synthesized by the same experimental procedure exhibit different microstructures and secondary phases (BaCuO_2 , BaCO_3) are found in $\text{GdBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and CuO in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. According to these preliminary results, the perovskite containing Nd is readily synthesized since the amount of secondary phases is much lower in that case. However, more work has to be done to ascertain the optimum thermal cycle for synthesizing these compounds.

FIGURE CAPTIONS

Figure 1 - Resistivity vs temperature curves for sintered pellets of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R = Y, Gd, Nd).

Figure 2 - X-ray diffraction patterns of sintered pellets for $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R = Y, Gd, Nd).

Figure 3 - Optical micrographies (1000 X) of the polished cross-sections of sintered pellets of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R = Y, Gd, Nd).

Figure 4 - Thermograms (DTA) of $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (R = Y, Gd, Nd) powders under oxygen atmosphere.

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TABLE I - CHARACTERISTICS OF THE SUPERCONDUCTING TRANSITION IN
 $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$

R	T onset (K)	Tc (midpoint) (K)	Tr=0 (K)
Y	92.0	91.0	88.0
Gd	93.5	92.0	90.0
Nd	95.0	94.0	93.0

RESISTIVITY (ARB. UNITS)





